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Single Crystal Growth of β-Al$_2$O$_3$ for Iso-Index Filters

by

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Single crystals of β-Al$_2$O$_3$ with a nominal composition of Na$_2$0.11 Al$_2$O$_3$ were grown from stoichiometric melts contained in an iridium crucible. Seeding was achieved from an Al$_2$O$_3$ single crystal. The growth axis was along a and X-ray data confirmed the unit cell parameters of a = 5.595 A and c = 22.531 A. The top and bottom lattice constants of the boules were equal to $\pm$ 0.002 A and indicated a fairly uniform composition. The measured density was 3.25 g/cm^3. The boules remained physically intact with no major cracks. However some cleavage progressed on the basal planes as determined by the appearance of interference fringes. Water vapor and CO_2 did not enhance the cracking. Crystals were stored in a desiccator but continued to cleave. Ionic diffusions of Na^{1+}, Ag^{1+}, Pb^{2+}, Rb^{1+}, Ca^{2+}, Cd^{2+}, Tl^{1+} were performed by immersion of β-Al$_2$O$_3$ into nitrate or chloride melts at temperatures of 360-740°C. The amount of exchange was

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Foreword

This final report describes research on the single crystal growth of β-Al_2O_3 and its possible applications to the construction of optical iso-index filters for the blue-green spectral region. The origins of this investigation are associated closely with preliminary research by Professor Oscar Stafsudd and his students at University of California at Los Angeles. The report contains all work performed during the period of August 1, 1990 to February 1, 1992. The issuing contract number was N00014-90-C-0006. The research was coordinated under Dr. Guy Beaghler, Code 12621, of the Office of Naval Research.

Preliminary work for this program began in the laboratories of Airtron Division of Litton Systems, Inc., 200 E. Hanover Ave, Morris Plains, NJ 07950. All research was under the direction of Dr. Roger F. Belt. The contracts main effort was performed at Airtron's production crystal growth facility at 1201 Continental Blvd., Charlotte, NC 28273. Mr. Mark Randles performed all of the ion exchanges and measurements. Mr. John Creamer grew all of the single crystals of β-Al_2O_3. Both were assisted by staff technicians of Airtron in special areas of growth or fabrication. Preliminary refractive index data were compiled by Prof. O. Stafsudd at UCLA. This report was prepared by Dr. Roger Belt, Mark Randles, and John Creamer. It was released for distribution in April, 1992.

1.0 Introduction

A communications system for satellite to a submerged submarine requires a laser, a narrow band high field of view filter, and an appropriate detector. The cesium resonance filter which operates at 455 or 459 nm is ideal but has suffered from a lack of a matched wavelength laser source. Another option is to design alternate laser schemes which position the wavelength at or near the maximum depth for 1/e loss in oceanic sea water types. This suitable range is 440-470 nm. In such a situation, one must design a matched filter which corresponds to the transmitting wavelength.

Polarization interference filters offer very narrow transmission bands, wide angular field of view, and tuning capability.[1] The Lyot-Ohman, Solc, various hybrids, and recent designs are powerful examples of technology employing common materials of single crystals of quartz, calcite, or ADP. A standard text[2] discusses some of the theory of optical wave propagation in these filters. Furthermore, the technologically superior iso-index filter ($n_0=n_e$ at particular λ) is introduced. Materials for iso-index filters are not common since they must be stable single crystals, high quality, and usually involve mixed ions in an isomorphous structure. The research group[3] at UCLA has shown that $\beta''-Al_2O_3$ fulfills these conditions in the Na-Ag system. However, $\beta''-Al_2O_3$ does not melt congruently[4] and large single crystals are not attainable readily.[5] An alternate superionic conductor, $\beta-Al_2O_3$, should behave similarly and can be grown as sizable (1x6 inch) boules.[6,7] This research details the growth of $\beta-Al_2O_3$ and its applications for iso-index filter use.

Single crystal $\beta-Al_2O_3$, with an approximate composition of $Na_2O \cdot 8Al_2O_3$, is a superionic conductor, i.e. it has a high electrical conductivity (1 $ohm^{-1}cm^{-1}$) in the solid state arising from the Na^+ mobility. Other ions can be exchanged for Na^+ by post growth diffusion without loss of optical quality. In this manner the electronic polarizability and hence, refractive index can be adjusted to formulate a crystal in which, at a particular composition and wavelength, n_0 may match n_e for this optically uniaxial

crystal. Such materials are called iso-index and compose the starting point for a highly selective filter. A good discussion is given by Adams.[8]

The central problem to be solved is the growth of reproducible single crystals of β-Al_2O_3. These should be high optical quality, sufficient size, uniform composition, correct orientation, and as readily available as any other optical material. The crystal grower faces two obstacles with β-Al_2O_3. It has a high melting point (ca 1950°C) which may be variable with composition and there is partial volatility of the Na_2O component during growth. In spite of these factors, crystals can be grown in boules nearly one inch diameter x 6-8 inches in length.

2.0   Experimental

2.1   Crystal Growth

2.1.1 Materials

The starting materials for this work were 5-9's purity sodium carbonate, 4-9's purity alumina powder, and flame fusion sapphire boules. Sodium carbonate was purchased from Johnson Matthey Aesar, Ward Hill, Massachusetts. The alumina powder was from Showa Denko K.K, Japan. The flame fusion sapphire was purchased from Rubis de Alps, Jarrie France.

2.1.2 Charge Preparation

The sodium carbonate needed for the charge was mixed with an equal weight of alumina powder. A portion of this mix is then placed in the bottom of the iridium crucible. Sapphire boule sections and chunks are than placed in the crucible. Finally the remaining powder mix is used to fill all empty spaces between the sapphire. All materials for a 750 gram charge were easily fitted into a 3"x3" iridium crucible. Reloading was done in a similar manner. Loading of the 4"x4" iridium crucible for the larger growth runs required some hot loading of the powder mix.

2.1.3 Growth Equipment

The beta alumina crystals were grown on our standard Czochralski crystal growth equipment. Features of the equipment include: a motor frequency power supply (operating frequency approximately 9-10 khz), a puller with fast and slow pull capabilities, adjustable crystal rotation from 3-65 rpm, and a flowing gas growth chamber with nitrogen/oxygen blending rotometers.

The crystal diameter was controlled using a proprietary computer system. The growth rate of the crystal is determined and subsequently controlled by taking periodic weight and time readings.

2.2 Fabrication of Material

To evaluate the as-grown beta-alumina boules several fabrication steps are required. Slices from the top and bottom of the boule were cut with a diamond ID saw to a thickness of 1-2mm. The crystal was also X-ray oriented at this step by measuring the deviation of a selected Bragg reflection relative to the sliced surface. The fixture holding the boule was than adjusted and another slice taken and remeasured until the boule is oriented. Accuracy of a few arc minutes is possible for both a-axis and c-axis cuts. The crystal is a hard, durable oxide and the same slicing conditions can be used as with other refractory oxides, such as YAG. A simple scratch test showed the Moh's hardness to lie between quartz and topaz or between 7 and 8.

The end slices are inspected for low angle grain boundaries in a polariscope. In general one large grain extended across the center of the slice with slightly misoriented grains on either side. The grain boundary planes are normal to the c-axis.

The boule slices were etched to remove sawing strain in preparation for precision lattice constant measurements with X-rays. A mixture of 1:1 phosphoric acid and sulfuric acid at 150-160°C is a selective etch which preferentially removes strained material in many oxide crystals. A two hour etch removes approximately 0.001 inch of slice thickness. The width of the Bragg peaks is 3 arc minutes which indicates good crystal quality.

Given beta-alumina's hardness of 7-8 it polishes like YAG. In fact YAG scrap material was used as "foot" material to surround the beta-alumina parts on a polishing fixture. Optical quality finishes are achieved by sequential lapping and polishing with boron carbide or alumina. The final polish was readily achieved with a 1.0 micron alumina slurry. The crystal's easy basal plane cleavage did not cause any problems.

Airtron fabricated prisms of the beta-alumina crystals with an included angle of approximately 45 degrees. The two sides on either side of this angle were optically polished to 10/5 scratch/dig and flat to 1/4 wave at 633nm. The included angle was precisely measured for use in subsequent calculations. The c-axis is parallel to the planes of these two sides.

2.3   Ion Exchange Procedures

The sodium in sodium beta-alumina is mobile and can be replaced with other ions by diffusion in molten salt baths. The crystal is not in an exact stoichiometric ratio of $Na_2O \cdot 11\,Al_2O_3$. There is an interstitial defect which accommodates additional sodium and oxygen in the conduction plane. The composition is best described [9] as $(Na_2O)_{1+x} : 11\,Al_2O_3$ or $Na_{1+x}Al_{11}O_{17+x/2}$ with $x = 0.24$. For monovalent cations virtually 100% of the sodium can be replaced. Divalent cations replace at most 50% of the sodium due to charge compensation. The formula for a divalent ion M^{++} would be $M^{++}_{(1+x)/2}Al_{11}O_{17+x/2}$. The maximum formula weights for 100% monovalent and 50% divalent substitution for sodium are quite different. The percent weight change is large enough to serve as a measure of the sodium replacement, especially for the more massive ions with high electronic polarizability expected to provide iso-index behavior.

The sequence of steps for the ion exchange procedure is given below:

- Select single grain portion of beta-alumina boule

- Slice into bars with 3-10mm thickness along the c-axis

- Wash and dry

- Weigh to 0.1mg

- Mount sample in a platinum basket

- Slowly insert and preheat sample in diffusion furnace

- Immerse in molten salt bath at 235-800°C depending on salt

- After the diffusion, slowly remove from furnace

- Clean and dry

- Weigh to 0.1mg

- Calculate weight change and repeat if desired

- Select samples for refractive index measurement

2.4 Measurements

2.4.1 X-ray lattice constants and density

The lattice constants for the hexagonal beta-alumina structure were measured with a precision Bond apparatus.[10] The revised X-ray wavelength for Cu Kα, is used with a value of 1.540611 angstroms. [11] at a Bragg angle of 55.7°. For the c-axis measurement we used the 24th order reflection of (00.1) at a Bragg angle of 55.1°. The X-ray density was calculated from the hexagonal unit cell parameters and the formula $(Na_2O)_{1+x}:11(Al_2O_3)$ with $x = 0.24$. There is one formula unit per unit cell. The calculated density is 3.258g/cc. The specific gravity of a section of this crystal was measured by immersion in water. After correcting for the density of water at room temperature the measured value was 3.253g/cc in very good agreement with the X-ray calculation.

2.4.2 Refractive Index

The refractive index measurements were performed by Dr. Oscar Stafsudd at the University of California, Los Angeles, using prisms fabricated by Airtron. The apparatus used to measure the refractive indices consisted of a small divided-circle spectrophotometer that was modified to accommodate an Ar-ion laser and various He-Ne lasers operating at wavelengths throughout the visible. The angle of the refracted beam was measured using the telescope and vernier of the spectrophotometer. Measurements

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of the refracted beam angle were taken at the minimum deviation condition.[12] At this condition the index of refraction, n', is given by

$$\frac{n'}{n} = \frac{\sin 1/2 (\alpha + \delta m)}{\sin \alpha/2}$$

where n is the index in air, δm is the angle of minimum deviation, and α is the angle of the prism.

3.0   Results and Discussion

3.1   Grown Crystals

The Czochralski growth of beta alumina proceeds readily from a melt once a seed has been obtained. A drawing of a typical furnace used for growth of a-axis boules at Airtron is shown in Figure 1. This arrangement employed a 3x3 inch iridium crucible for growing a 1.0-1.5 inch diameter boule. A similar arrangement was constructed for a 4x4 inch crucible in order to demonstrate 2 inch diameter growth capability. During the course of this program, fourteen growth runs were completed. These are summarized in Table 1 in chronological order.

In the first run, B32-352, crystal growth was initiated on an iridium wire dipped into the melt. A nearly single crystal was produced with a growth direction very close to an a-axis. Seeds were cored from this crystal and used for seeding subsequent runs.

The best conditions for growth from a 3"x3" iridium crucible appear to be: 3mm/hour pull speed, 5 rpm crystal rotation, an atmosphere of nitrogen with 1.0% oxygen, and a melt composition of seven moles of Al_2O_3 to one mole of Na_2O. A-axis seeds were used for all growth runs. The crystals grown from the 3"x3" crucible were 1.0" to 1.2" in diameter and 2.0" to 3.0" long.

Crystal B32-379 was grown with more sodium in the melt. The crystal grew easily and exhibited good shape and diameter control. Examination of the crystal with a high intensity light beam, however, revealed a high scattering site density.

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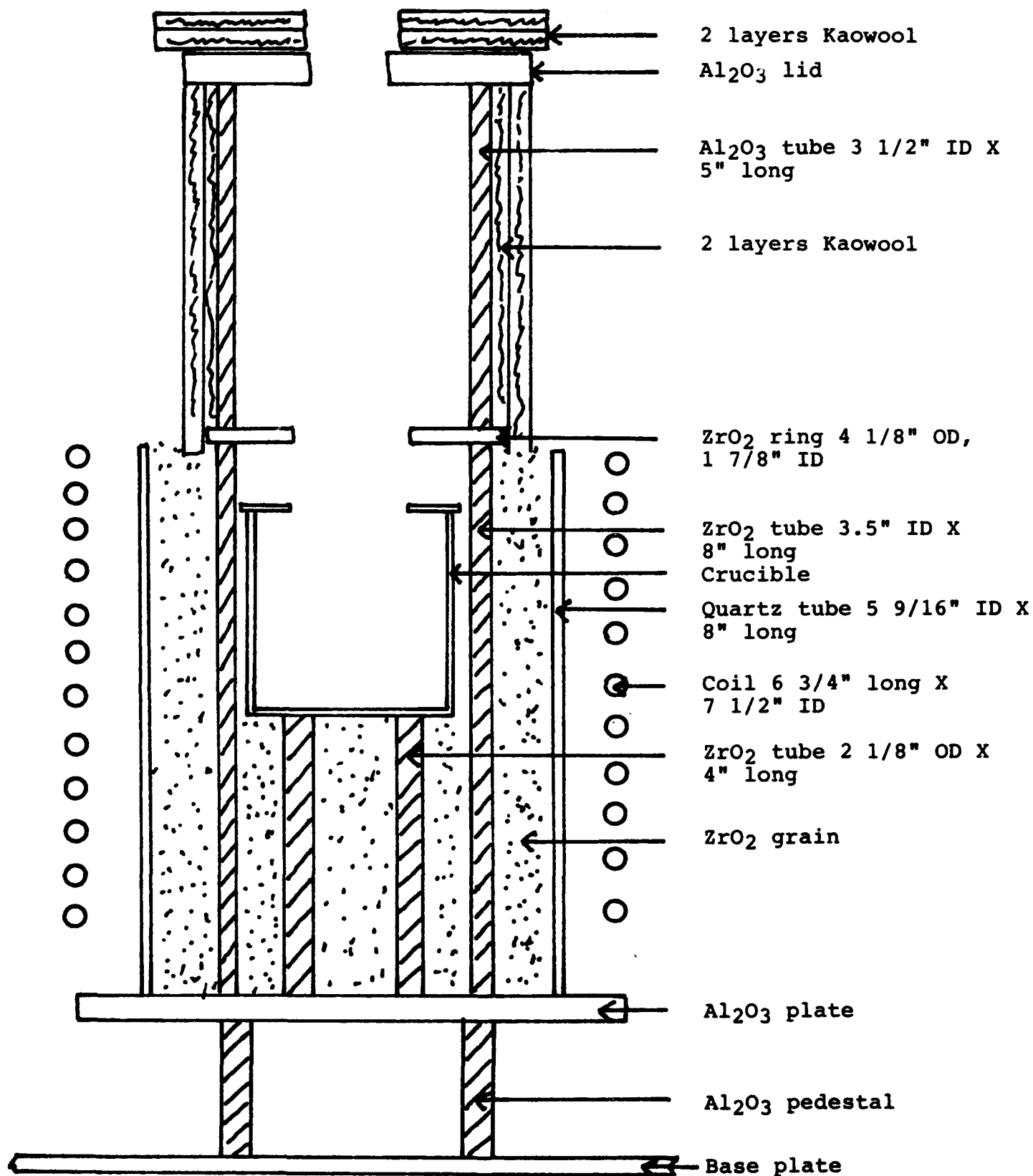
Figure 1 Typical Furnace for Beta Alumina Growth in 3 x 3 Inch Crucible

The labels in the figure read:

- 2 layers Kaowool
- Al_2O_3 lid
- Al_2O_3 tube 3 1/2" ID X 5" long
- 2 layers Kaowool
- ZrO_2 ring 4 1/8" OD, 1 7/8" ID
- ZrO_2 tube 3.5" ID X 8" long Crucible
- Quartz tube 5 9/16" ID X 8" long
- Coil 6 3/4" long X 7 1/2" ID
- ZrO_2 tube 2 1/8" OD X 4" long
- ZrO_2 grain
- Al_2O_3 plate
- Al_2O_3 pedestal
- Base plate

Table 1   Beta-Alumina Growth Run Summary

Crystal Number	Melt Composition $Na_2O:Al_2O_3$	Atmosphere $\%O_2$	Changes	Results	Run No.
1	1:7	1.0	standard 3x3 furnace	Beta phase, seed boule	B32-352
2	reload	1.0	same	not beta phase due to reload with 1:7 comp	B32-353
3	1:7	1.0	same	2.8cm diam x 5.2cm, facets on shoulder	B32-358
4	1:7	1.0	increase temp gradient by removing baffles	2.5cm x 8.3cm, no change in shoulder shape	B32-359
5	1:7	1.0	same furnace, try "cold" start	3.2cm x 5.3cm, rounder shoulder but cracked at top	B32-369
6	reload	1.0	same furance	3cm x 6.3cm, seed boule	B32-370
7	1:7	2.0	higher oxygen	2.5cm x 4.4cm	B32-371
8	1:5	1.0	more Na_2O	2.5cm x 5cm, many scattering sights	B32-379
9	1:7	1.0	added baffles to furnace	2.5cm x 5cm, twin, pronounced c-axis facets down boule	B32-380
10	reload	1.0	same as #9	3cm x 5cm, best quality boule to date	B32-381
11	reload	1.0	same as #10	3cm x 7.5cm, fair quality	A13-137

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Crystal Number	Melt Composition $Na_2O:Al_2O_3$	Atmosphere $\%O_2$	Changes	Results	Run No.
12	1:6:5	1.0	4x4 crucible furnace with baffles	5.6cm x 7cm, similar quality as the smaller crystals	A12-222
13	1:7	1.0	4x4 crucible furnace with baffles	5.3cm x 7cm, large single grain down center	B32-411
14	reload	1.0	same as #13	no crystal, alumina seed rod& baffles decomposed	B32-412

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Increasing the oxygen content in the growth atmosphere to 2.0% as in run B32-371 gave no noticeable improvement. The best improvement in crystal quality seemed to come from reductions in temperature gradients. The use of zirconia baffles to lower the vertical temperature gradient reduced the incidence of cracking. The best looking beta alumina crystal grown during this work, B32-381, was grown using a furnace with the baffles.

Crystals A12-222 and B32-411 were grown from a 4"x4" iridium crucible. These crystals were over 2.0" in diameter and about 2.5" in length. The quality of these crystals was comparable to the smaller ones, but they appear to have more scattering sites.

The beta alumina growth runs were terminated by raising the crystals with the fast pull motor high enough to separate them from the melt. The crystals were then cooled to room temperature over several hours.

Typical crystals one inch diameter grown under this contract can be seen in Figures 2 and 3. The most common defect found in all of the crystals are longitudinal surface cracks. Other defects include: grain-boundaries, twinning, bubbles, and massive cracking.

X-ray lattice constants were measured on samples from the top and bottom of the first beta-alumina boule (B32-352). The results were:

top of boule	$a = 5.595$ Angstrom
top of boule	$c = 22.531$
bottom of boule	$c = 22.532$

These agree well with standard powder diffraction file data. The bottom value shows that the lattice spacing does not vary significantly during growth.

Several problems are associated with the growth of beta alumina. There is a constant loss of Na_2O during the growth process. The use of an atmosphere containing oxygen helps to reduce this loss, but if the growth is not carried out in an expeditious manner, single crystals of the beta phase cannot be grown.

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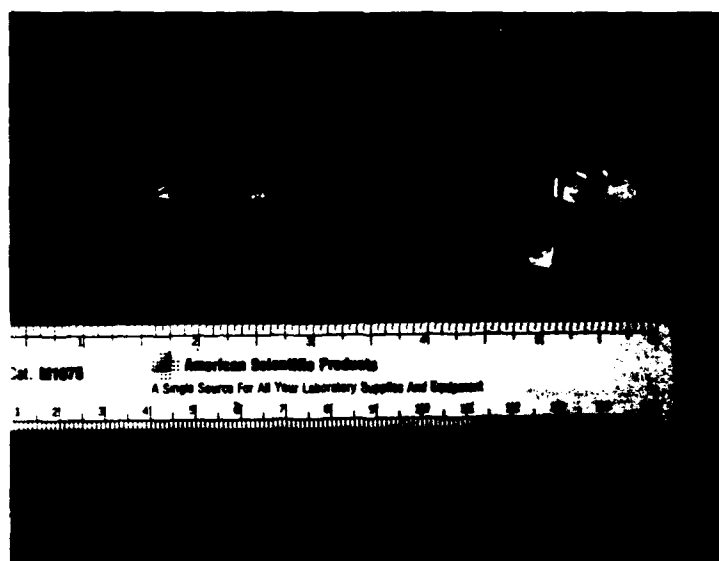Figure 2   One inch boule of β-Al$_2$O$_3$, Run 8. B32-379.

Figure 3   One inch boule of β-Al$_2$O$_3$, Run 11, A13-137

Care must be taken in selecting the materials used for furnace construction. We found that alumina ceramics even when used in the lower temperature regions of the furnace are eroded by the Na_2O vapor. Zirconia oxide works well.

The longitudinal cracks and twinning seem to be difficult and persistent problems arise. The twinning may be overcome by getting better single crystal starts. Steepening the temperature gradients to facilitate this, however, increased the loss of Na_2O and also seemed to create a cracking problem.

Some improvement in the longitudinal cracking might be expected if aluminum oxide and sodium carbonate were reacted in such a manner that all residual moisture and carbon dioxide were removed.

The last three runs of our program involved the growth of two inch diameter boules. One of these is pictured in Figure 4. It contained few cracks in the boule upon cooling. This run however, when sliced to yield an a-axis section, showed several large angle grain boundaries. Obviously these arise from the seed and propagate down the boule where they become more exaggerated. Figure 5 shows one example.

3.2 Crystal Stability and Storage

Beta-alumina does not absorb water. A piece of crystal was soaked for 2.5 days in tap water. The weight before and after was carefully measured to 0.1mg. The weight change if any was less than 0.01%. However, as a precaution crystals were stored in a desiccator with a commercial "Drierite" calcium sulfate desiccant.

As-cut crystal slices develop cracks along the c-axis cleavage planes during storage. After 1-2 weeks sliced parts show new cracks whether stored in a desiccator or in the lab ambient. A flowing nitrogen desiccator box slowed by did not prevent the crack formation. Figure 6 shows slices held in nitrogen (#4-2) and "Drierite" (#4-3) in the as-cut condition and after a ten day period. Both developed cleavage cracks.

It is possible that another atmospheric gas contributes to the time-dependent cleaving and the likely candidate is carbon dioxide CO_2. The sodium oxide in the crystal
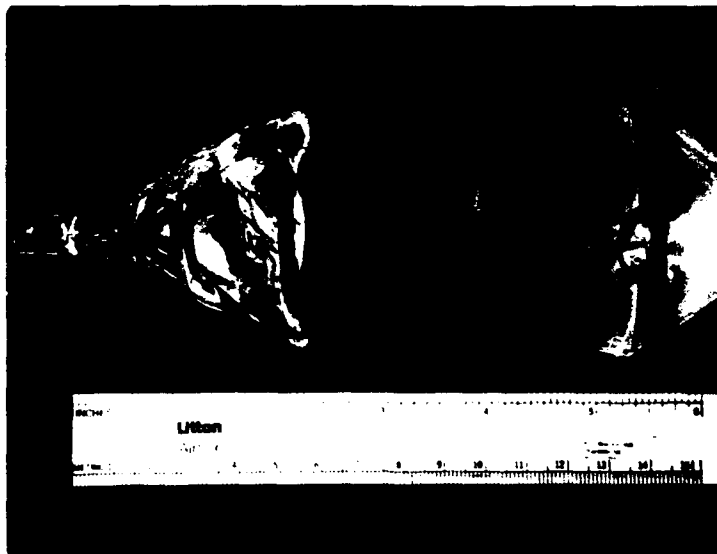
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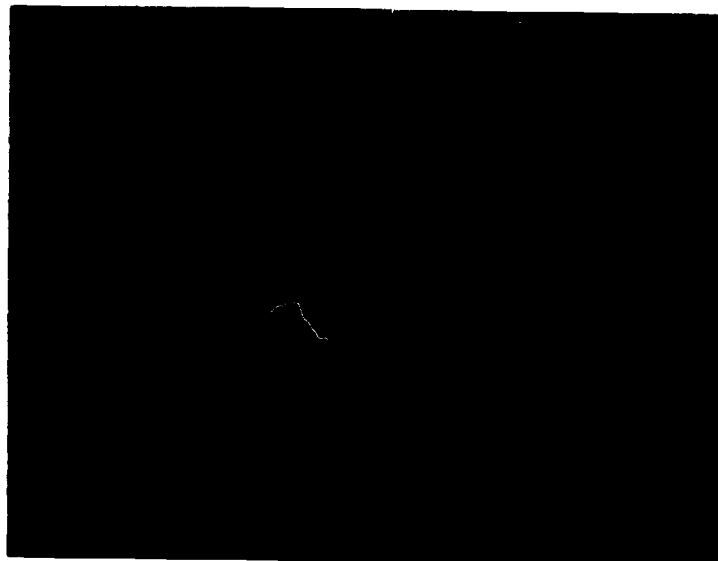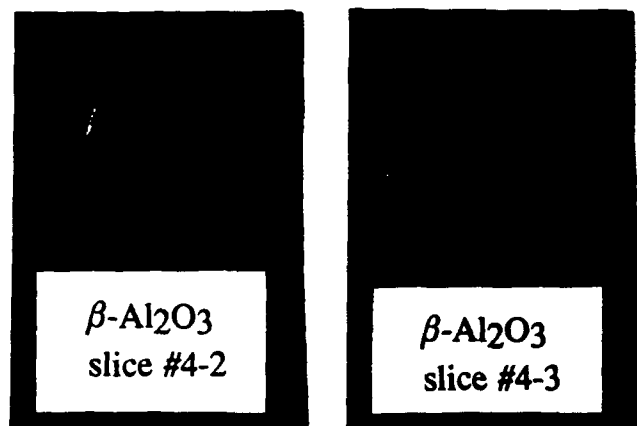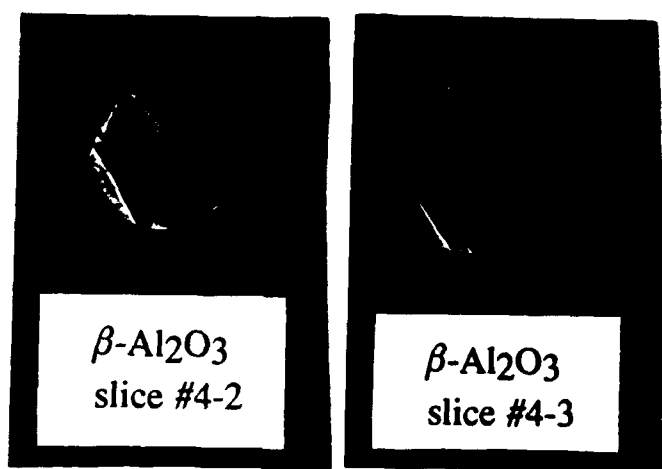Figure 4   2 inch diameter boule of a-axis β-Al$_2$O$_3$, A12-222

Figure 5   A-axis section viewed between crossed polarizers, A12-222

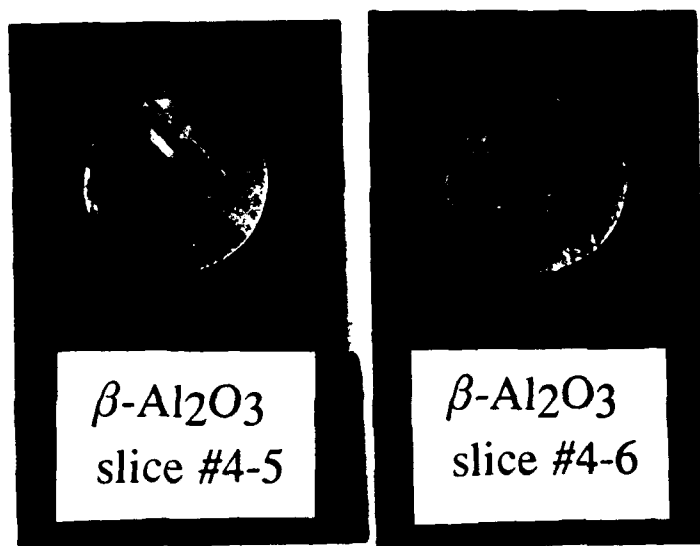As-cut slices

10 days later

Figure 6   Spontaneous cracking of beta-alumina slices
Sample #4-2 kept in dry nitrogen and #4-3 kept in "Drierite" dessicator

to the extent that it behaves as free Na_2O should combine with CO_2 to form sodium carbonate Na_2CO_3. Formation of the carbonate at the surface could pry apart the cleavage planes resulting in the cracks. Pellets of potassium hydroxide KOH were added to the "Drierite" dessicator because KOH readily absorbs CO_2.

The cracks that develop in thin slices can also be seen in whole boules, but boule cracks propagate with a time scale of months rather than days. In either case the cracks seem to originate at small surface cracks of cleavage present on the as-grown boule surface. We did an experiment in which an as-cut wafer (#4-5) was etched in 1:1, phosphoric: sulfuric acid for two hours at 150C. This is a selective etch that should relieve strain due to cracks or saw damage. A control wafer (#4-6) cut at the same time was not etched. Both wafers were photographed to document the location of a few cleaves originating from the boule stock, see Figure 7. After 23 days in the KOH and "Drierite" dessicator the etched wafer had no additional cracks or cleaves while the unetched one fell into six pieces with many more cleaves visible. The remarkable improvement must be due to the etching because the KOH added to the dessicator had not prevented the unetched wafer (#4-6) from deteriorating. These two test wafers were then placed in lab ambient to observe the stability of the etched piece. After several weeks the etched wafer (#4-5) had developed cleaves and cracks similar to the unetched control wafer. While the stability of the etched wafer did not probe to be a complete solution to the problem it may provide clues to the origin of the cracking.

3.3   Ion Exchanges

Ion exchanges in $\beta-Al_2O_3$ single crystals are possible for all monovalent cations, most divalent cations, and small amounts of some trivalent cations such as the smaller radii rare earths. The ion exchanges were carried out in fused salts as explained in the experimental section. The measured amounts of cation exchange can be calculated by appropriate weight changes in the single crystal. For example, Table 2 gives some calculated data for selected ions that we have experimented with during this program.

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As-cut slices
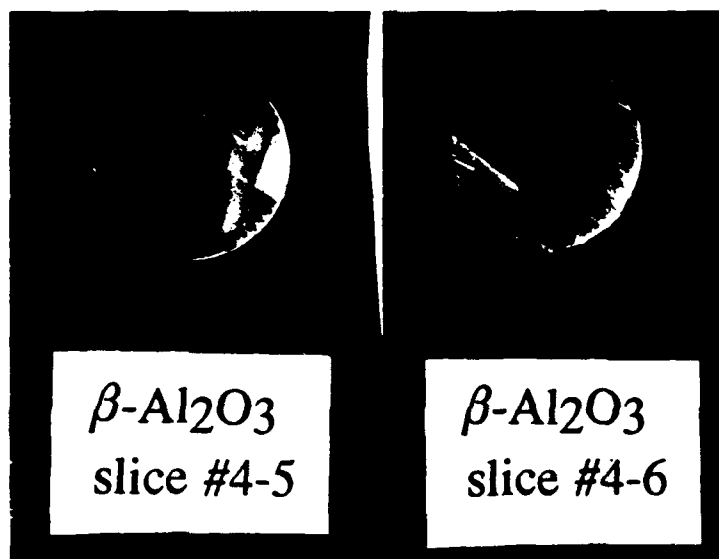
23 days later

Figure 7   Etching reduces cracking of beta-alumina slices
#4-5 etched and #4-6 unetched, both kept in KOH & "Drierite" dessicator

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Table 2   Calculated Formula Weights for Beta-Alumina Diffusions Replacing Sodium

Monovalent: $M^+_{1+x} Al_{11}O_{17+x/2}$ with x = 0.24

Divalent: $M^{++}_{(1+x)/2}Al_{11}O_{17+x/2}$ with x = 0.24

Ion in β-Al$_2$O$_3$	Maximum substitution for sodium %	Formula Weight	Weight change for full substitution %
Na$^+$	100	599.22	0
Rb$^+$	100	676.69	12.9
Ag$^+$	100	704.47	17.6
Tl$^+$	100	824.15	37.6
Ca^{++}	50	595.56	-.06
Cd^{++}	50	640.41	6.9
Ba^{++}	50	655.86	9.5
Pb^{++}	50	699.17	16.7

The fused salts were typically chlorides or nitrates of the ionic diffusant. In general the nitrates work better because of the lower melting temperatures and lower evaporation rates. These tests employed platinum crucibles, but glass or fused silica beakers could be substituted for the nitrates.

The diffusion proceeds exclusively along the (00. 1) conduction plane and this thickness was typically 3-10mm. No attempt was made to determine the kinetics of the diffusion as this has been previously reported.[13] Instead we sought the highest fractional substitution via long diffusion times in order to obtain samples of end-member compositions for the refractive index measurements.

Table 3 lists the monovalent cation diffusion results. The Na diffusion produced no change in weight implying that the as-grown boule contains the full complement of sodium. Ag^+, Rb^+, and Tl^+ all diffused to nearly 100% replacement and provided material for refractive index measurements. Diffusions of Cs^+ were not attempted because Yao and Kummer (1967) reported[13] great difficulty incorporating more than 20% Cs due to its large size. Diffusion run Rb-3 resulted in 40% sodium replacement after 23 hours which agrees with the equilibrium value reported by Yao and Kummer (1967) for a 1:1 Rb:Na melt. $TlNO_3$ in highly recommended over TlCl because of the negligible evaporation loss.

Table 4 shows the results of the divalent cation diffusions. In general these ions diffuse more slowly and in the case of barium not at all. The $CaCl_2$ bath actually etched the beta-alumina surfaces and the other divalent ions caused numerous cracks in the samples. These results agree with Yao and Kummer (1967) who reported cracking in all divalent cation diffusions. None of the divalent diffusions generated materials of sufficient quality for index measurements.

3.4   Refractive Index Data

After cation exchanges were performed on single crystal pieces of β-Al_2O_3, prisms were cut and polished for refractive index measurements by the minimum

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Table 3   Monovalent Cation Diffusions

Sample	Ionic Melt	C-axis Length (mm)	Temperature (C)	Time (Hour)	Weight Gain (%)	Sodium Substitution (%)
Na-1	NaNO$_3$	4	360	24	0	100
Ag-1	AgNO$_3$	4	320	24	17.40	99
Ag-1 continued	AgNO$_3$	4	320	24 (48 total)	17.46 total	99
Rb-1	RbCl	9	740	18	12.1	94
Rb-2	RbCl	9	740	20	12.7	98
Rb-3	1:1 atomic RbCl:NaCl	6	680	5.5	3.9	30
Rb-3 continued	1:1 atomic RbCl:NaCl	6	680	23 total	5.1	40
Tl-1	TlCl	10	440	16	24.2	64
Tl-2	TlCl	10	440	33	31.9	85
Tl-3	80:20 TlCl:NaCl	---	---	---	---	excessive TlCl vaporization
Tl-4	TlNO$_3$	9	235	24	8.3	22
Tl-5	TlNO$_3$	10	350	88	---	cracked, no weight
Tl-6	TlNO$_3$	6	350	88	---	cracked, no weight
Tl-7	TlNO$_3$	3	350	90	36.2	97

Table 4 Divalent Cation Diffusions

Sample	Ionic Melt	C-axis Length (mm)	Temperature (C)	Time (Hour)	Weight Gain (%)	Sodium Substitution (%)
Pb-1	$PbCl_2$	9	570	70	10.6	63
Pb-2	$PbCl_2$	9	540	4	1.2	7
Ca-1	$CaCl_2$	8	800	16	-1.9	etched surfaces
Ba-1	62:38 $Ba(NO_3)_2$: $BaCl_2$	9	540	17	0	0
Ba-2 continued	62:38 $Ba(NO_3)_2$: $BaCl_2$	9	540	111 total	0	0
Cd-1	$CdCl_2$	9	580	5	1.3	19
Cd-2	$CdCl_2$	9	580	31	0.7	10
Cd-3 continued	$CdCl_2$	9	580	59 total	0.9	13

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deviation method. Table 5 summarized he refractive index results in terms of the birefringence, n_e-n_o. The as-grown sodium beta-alumina has negative birefringence in the visible as does the rubidium sample. Silver is still negative but with a smaller magnitude. Thallium has only a small positive birefringence but this is very significant because it means that an iso-index point (n_e=n_o) exists at some wavelength in the visible. The iso-index wavelength will be a function of the thallium concentration in the crystal and should be adjustable.

In Table 6 we summarize some measurements carried out quantitatively by Prof. O. Stafsudd and his students on prisms fabricated at Airtron. The prism angle, α, was also measured by them. The thallium data are to be noted particularly.

3.5   Problem Assessment

Boule Stability

Thin slices with a thickness of 1-2mm in the c-axis direction develop cracks in a lab atmosphere with time scale of days or weeks. Apparently a reaction takes place on the basal planes which pushes them apart. One proposed mechanism is CO_2 absorption by the sodium in the crystal. Replacement of the sodium by diffusion may solve the problem. In fact the small crystal samples used for the diffusion of silver, rubidium, cadmium and thallium have been kept for months in a lab ambient without developing the basal plane cleavages. These samples were 4-10mm thick in the c-axis direction but the lack of cracking cannot be attributed solely to the increased thickness.

Iso-index filters made from a crystal such as beta-alumina will be on the order of centimeters in each dimension and the spontaneous cleavage will be less likely. If necessary the edges of these crystal blocks could be treated to prevent gas permeation by thin film coatings of various types.

Future Diffusion Investigation

Thallium has been shown to provide the necessary change in the birefringence for iso-index behavior. For the development of practical filters a number of diffusion runs

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Table 5   Birefringence of Diffused Beta-Alumina Crystals
$Na_{1+x} Al_{11} O_{17+x/2}$ with $x=0.24$

Diffusant Ion	Percent Substitution for Na	Birefringence $n_e - n_o$
Na^+	100	large negative
Rb^+	94	large negative
Ag^+	99	small negative
Tl^+	85	small positive

Table 6   Index of Refraction Measurements

Samples (Beta Alumina Prisms)		Red (HeNe) 632.8	Green/Blue 488 (Argon) 514.5	Yellow (HeNe) 594	Orange (HeNe) 604/612	λ (nm)
Silver Diffused α = 45°	n_e	1.64	1.67	1.68		
	n_o	1.67	1.73	1.79		
40% Rubidium α = 44° 21'	n_e	1.62	1.64			
	n_o	1.65	1.66			
Rb - Diffused α = 42° 43'	n_e	1.66	1.68			
	n_o	1.68	1.69			
Undiffused (Na) α = 44° 50'	n_e	1.63	1.62			
	n_o	1.66	1.67			
Thallium Diffused α = 37° 57'	n_e	1.75	1.781 (G) 1.789 (B)	1.761	1.759	
	n_o	1.7	1.728 (G) 1.746 (B)	1.722	1.718	

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need to be performed which will determine the iso-index wavelength where $n_e=n_0$ as a function of thallium concentration in the crystal. Diffusion baths can be prepared with varying ratios of $TlNO_3$ and $NaNO_3$. For each bath it will be necessary to determine the time required for the sodium to be uniformly replaced by thallium. This time will be a function of the distance from the center of the diffusion plane to the edge of the crystal. For each equilibrated sample the refractive indices would need to be measured and the iso-index wavelength determined.

3.6   *Theory and Calculations*

In this section we provide a minimum of the theory for an iso-index filter to understand the objectives, calculations, and possible applications for β-Al_2O_3 single crystal. The interested reader is referred to the thesis by Adams[8] for a more exhaustive treatment.

Let us define the isotropic or iso-index point at a given wavelength by λ_c. The birefringence (n_e-n_0) near the isotropic point λ_c can be expanded in a series and represented by equation (1)

(1) $N_e\text{-}n_0 = \alpha\,(\lambda\text{-}\lambda_c) + \ldots\ldots$

where n_e and n_0 are the extraordinary and ordinary refractive indices for a proposed uniaxial material. The rate of dispersion of the birefringence near λ_c is given by α where

(2) $\alpha = \partial\,\Delta n/\partial\,\lambda$

The phase retardation (T) of a crystal plate of thickness (d) is then given by

(3) $T = 2\pi\dfrac{\alpha}{\lambda}\,(\lambda-\lambda_c)\,d$

By definition, the crystal optically is isotropic at λ_c and the phase retardation is zero, i.e. the plate is a zero order waveplate for λc. This fact is based on the isotropic nature of the material at λ_c and not on any specific path length through the material, as may be the case for a Lyot-Ohman type filter. Thus only for the iso-index condition is there independence of the angle of incidence.

The bandwidth of an iso-index filter depends on the rate of dispersion of the birefringence and is given by

(4) $\Delta\lambda_{1/2} = .886\ \dfrac{\lambda}{2|\alpha D|}$

where D is the thickness of the thickest plate. For a given value of D, the bandwidth is inversely proportional to α, i.e. the smaller the dispersion of the birefringence, the narrower is the bandwidth.

The angular variation of the bandpass is given by

(5) $\Delta\lambda_{1/2}(\phi) = \Delta\lambda_{1/2}\left[\dfrac{1-\sin^2\alpha(1-2\cos^2\phi)}{2n^2}\right]^{-1}$

The most important feature of the iso-index filter is its large field of view. In the isotropic condition the peak transmission at λ_c is independent of the angle of incidence. This is not strictly true for the bandwidth. Even with this slight variation, the bandwidth can maintain Angstrom dimensions. Thus the iso-index filter is highly beneficial where a weak signal must be retrieved from a strong spectrally local noise source. A good example is a green laser to be detected in the presence of sunlight.

Figure 8 illustrates some field of view characteristics of a Lyot-Ohman iso-index filter. Curve 1 is for an extreme angle of index (θ-90°) with a plane of incidence parallel to the c-axis of the plates (ϕ-90°). Curve 2 is for normal incident light. Curve 3 is for the same extreme angle of incidence (θ-90°) but with plane of incidence perpendicular to the c-axis of the plates (ϕ-0°). The curves in Figure 8 were calculated by the UCLA group.

Consider now an array of several iso-index plates of random thickness, D, each separated by parallel polarizers as illustrated in Figure 9. Transmission through such a system occurs when polarized light traveling through the crystal plate array experiences no modification of its polarization. This is the zero wave plate condition, and only occurs at the iso-index wavelength λ_c. At every other wavelength a zero wave condition
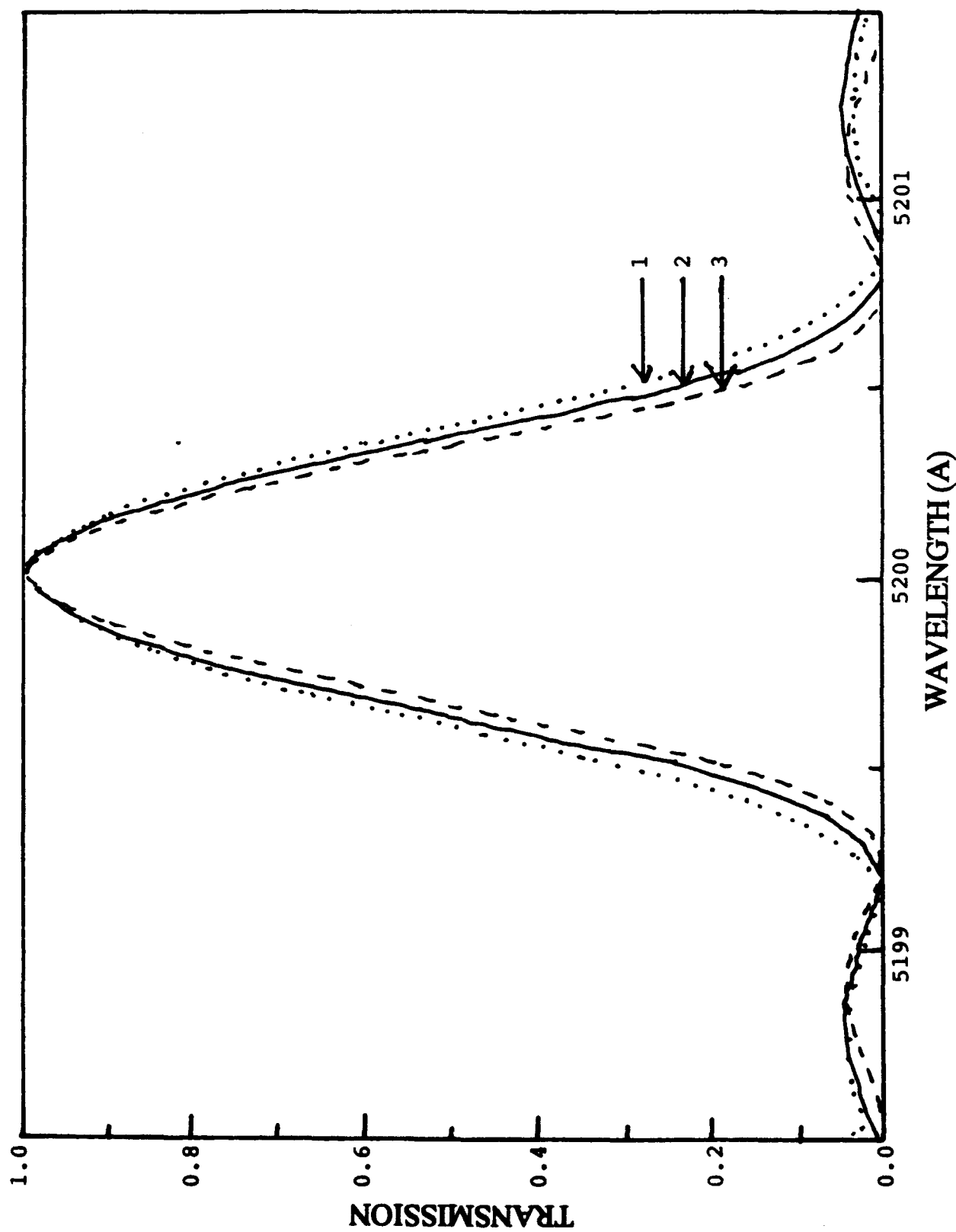
Figure 8   Field of view characteristics of a Lyot-Ohman iso-index filter

Polarizers   Iso-Index Plates
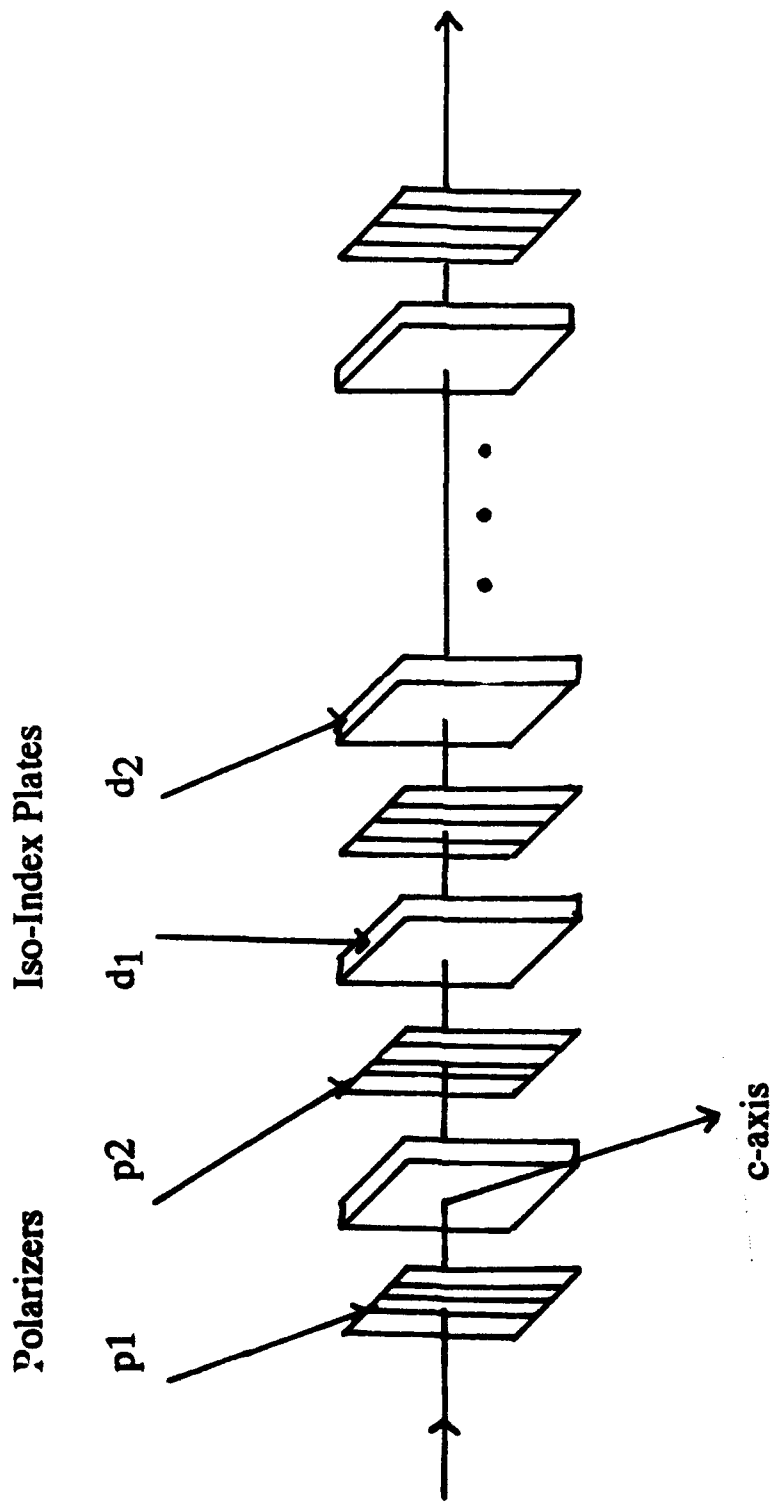
p1

p2

d1

d2

c-axis

Figure 9   Schematic of Iso-Index Filter

arising from path length through the crystal is experienced for every plate in the array. Obviously, an array of randomly thick crystal plates will not likely exhibit such a condition, thus leaving only the iso-index wavelength to transmit through the filter.

4.0 Conclusions

This work has demonstrated the growth of one inch diameter single crystals of β-Al_2O_3 in the a-axis configuration. Although cracking and local misorientations of the boules does occur, the causes are unknown and not associated with H_2O or CO_2 uptake. It appears that some material is stable and can be cut, polished, and ion diffused without mishap. We have grown two inch diameter boules which contain large sections free of grain boundaries. The ion exchange studies have shown that Tl^{+1} can be substituted for Na^{+1} with the result that an iso-index crystal system is possible. Ion exchanges were performed with many univalent and divalent ions. Refractive indices were measured on several key materials. The next step in this program would involve the actual construction of a prototype filter from appropriate materials.

5.0 Recommendations

A major impediment to the use of β-Al_2O_3 as an optical material is the spontaneous cracking on basal planes. An effort to solve this problem would be worthwhile since other parts of our program were successful. Thus ion diffusions can be performed to attain iso-index materials with Tl. The actual construction of a filter was not a part of our program. However, even with present material it would be useful to design and construct a filter for a specified wavelength. Such a device would be useful in further studies. It should also be stressed that other mixed crystal compositions can lead to iso-index behavior. The awareness of these in an ideal system would lead to practical filters.

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June 10, 1992

To: Those Concerned

Re: *Single Crystal Growth of β-Al$_2$O$_3$ for Iso-Index Filters*

by R.F. Belt, M.H. Randles, and J.E. Creamer

Enclosed you will find page iii of the above named final report. Would you please insert this page into your copy (s), as it was left out by mistake.

Thank you.

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measured by weight increase. The X-ray lattice constants were also measured for the exchanged crystals. The Ag^{1+} exchanged material was light stable when tested with 10^4 shots of a 308 nm excimer laser. All of the divalent ions gave exchanged crystals which cracked more easily than the original β-Al_2O_3. These appeared to be tension related since lattice constants increased markedly. To achieve iso-index matching in the visible, the diffusing ions should possess high electronic polarizability. Pb^{2+}, Cd^{2+}, Tl^{1+} satisfy this requirement. The Tl^{1+} works best because of charge, size, and index change. Single crystals of the exchanged materials were cut and fabricated into prisms. Their refractive indices were measured by the meth $\cdot$ of minimum deviation. The Na^{1+}, Rb^{1+}, Ag^{1+} crystals were all uniaxial negative $(n_e < n_o)$. Measurements were not obtained on Ca^{2+}, Cd^{2+}, Pb^{2+}, and Ba^{2+} because of cracking. The Tl^{1+} ion exchanged material is uniaxial positive and when combined with Rb^{1+} or Ag^{1+} offers the best hope for an iso-index material in the visible. We discuss the theory for an iso-index filter and calculate the bandpass, angular variation of bandpass, and field of view characteristics of a Lyot-Ohman filter. The construction of such a filter is explained with the use of exchanged β-Al_2O_3.